



GREENTECH PARTNER SOLUTIONS LLC.

DIRECTOR'S OFFICE
DEPT OF TOXIC SUBSTANCES CONTROL

JUL 10 2014

RECEIVED

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To: DEBBIE RAPHAEL, Director
Department of Toxic Substances Control
Safer Products and Workplaces Program
P.O. Box 806. Sacramento, CA 95812-0806

Safer Products & Workplaces Program

Sent via US MAIL

JUL 10 2014

Dear Ms. RAPHAEL,

Department of Toxic Substance Control

I would like to thank you for taking time to get introduced with this letter. California Department of Public Health recently issued a letter, supported by The Governor of the State, Mr. Edmund G. BROWN Jr. regarding toxic Isocyanates: Work safely sheet. We are registered with U.S. Green Building Council local Bay Area Company made scientific breakthrough in coating and paint industry with a solution to none toxic isocyanate products. Our Company introduces a new patented non toxic non-isocyanate hybrid polyurethane product line. It's called Green Polyurethane™ and it's the first polyurethane-based commercialized coatings and paint that is a "hybrid epoxyurethane." In other words, it does have some epoxy in it, but the properties have been enhanced through a patented process that gives it the durability and chemical structure of polyurethane without using any isocyanates. We also work on commercialization of non isocyanate foam. The product has been highly recognized by the EPA and was a finalist for the American Chemistry Council Polyurethane Innovation Award. We offer to provide the alternatives to toxic isocyanate materials currently are in use in the State of California.

As we all know, on June 25, 2013 the Occupational Safety and Health Administration (OSHA), a division of the US Department of Labor, initiated a National Emphasis Program to protect workers from serious health effects from occupational exposure to isocyanates. Isocyanates are found in polyurethane based products. According to OSHA, "Workers exposed to isocyanates can suffer debilitating health problems for months or even years after exposure which could result in death." The US EPA (Environmental Protection Agency) is looking to control and potentially outright ban isocyanates and mentioned Hybrid's technology as an alternative to toxic polyurethane in its Action Plan against isocyanates (see page 4 Figovsky and Shapovalov) <http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/mdi.pdf>

We are asking for your attention to this matter to help us to increase legislative bodies/public awareness for the existence of the product that can be used as an alternative to the currently used toxic isocyanates in making polyurethane.

If this project would be in the area of your interest we would be happy to meet you and establish mutually beneficial relationships with local GOVERNMENT for working together toward better environment. Sometimes this month we will be in Sacramento meeting with EPA and would like to invite you, or your Agency representative for presentation and introduction. Please reply for more details. My number is 650-4913449 ext 6 or via email:

[Vaulin@greentechpartnersolutions.com](mailto:vaulin@greentechpartnersolutions.com)

*Thank you for your attention to this matter.
Regards*

VAULIN Max V.
CEO/ Greentech Partner Solutions LLC.



RON CHAPMAN, MD, MPH
Director & State Health Officer

State of California—Health and Human Services Agency
California Department of Public Health



EDMUND G. BROWN JR.
Governor

June, 2014

Dear Health and Safety Manager:

The California Department of Public Health, Hazard Evaluation System and Information Service (HESIS), announces its new Fact Sheet on Isocyanates, a chemical component of polyurethane paints, foams, packaging, adhesives, and other products. We are enclosing a copy of this publication, entitled **Isocyanates: Working Safely**.

The main health points include:

- Isocyanates can sensitize workers (cause allergy), producing asthma and skin disorders.
- Workers with occupational asthma from isocyanates can react to very low levels of exposure (even below exposure standards), and may need to change jobs permanently.
- Good work practices and proper use of protective equipment can help prevent isocyanate health effects.

To produce this Fact Sheet, HESIS staff talked with medical experts, industry and union representatives, employers and small business owners to ensure that the document is up-to-date, practical, and informative. This Fact Sheet reflects significant changes in isocyanate / polyurethane technology, as well as advances in the state of medical knowledge. We conclude that caution is still called for in the use of these products. Potential action items for you as an employer include:

- Train your workers about the health hazards of uncontrolled exposure to isocyanates.
- Develop an isocyanate safety plan for your workplace, and implement it.

Should you need additional hard-copies of this Fact Sheet, please call the HESIS Publication Line toll-free at (866) 627-1586, or fax your request to (510) 620-5743. The publication is also available in electronic format at: <http://www.cdph.ca.gov/programs/hesis/Documents/Iso.pdf> For specific questions, HESIS maintains a Workplace Hazard Helpline at (866) 282-5516.

Sincerely,

Dennis Shusterman, MD, MPH
Chief, Hazard Evaluation System and Information Service

OCCUPATIONAL HEALTH BRANCH

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GREEN POLYURETHANE™

The first polyurethane-based coatings and paint which eliminate the use of all toxic isocyanates from the entire production process

- Zero Isocyanates, ~Zero VOC
100% solids, minimal odor
- 2 times more durable than
conventional polyurethane-based
coatings and paint
- Cost savings of up to 45%
- High gloss, self priming - achieve
any thickness in one coat

THE DANGERS OF ISOCYANATES

Isocyanates are potential human carcinogens used in conventional polyurethane-based coatings and paint which are hazardous to one's health and to the environment. Isocyanates can cause irritation of skin and mucous membranes, chest tightness, difficult breathing, upset stomach, fevers and prolonged exposure has been known to cause severe asthma and even death.

HYBRIDCOATINGTECH.COM



FEATURES & ADVANTAGES OF GREEN POLYURETHANE™

- Zero toxic isocyanates, ~ Zero VOC, 100% solids, minimal odor:
 - > Avoid costly application safety measures such as HVAC shutdown, extra ventilation, weekend work, displacement of workers or students and business stoppages in adjacent application zones, thereby reducing application costs 30 – 60%
- 2 times better wear resistance and 10-30% higher adhesiveness
- Only 1 coat needed due to 100% solids, specific curing formulation (depending on substrate)
- Improved corrosion resistance
- Improved resistance to chemical degradation
- Safe & easy curing in cold, hot or sunny conditions

APPLICATIONS

Green Polyurethane™ coatings and paint can be applied to almost any surface and is particularly useful on concrete and metal in heavy traffic and corrosive surface areas. Typical applications include:

- industrial and commercial buildings and garages
- food processing facilities
- medical and pharmaceutical clean rooms
- marine applications
- equipment for liquid fertilizer delivery
- protective coatings inside pipes
- military applications

Hybrid Coating Technologies (HCTI.OB) is a San Francisco-based innovator focused on improving the quality and safety of coatings and paint for customers around the world.

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Recent advances in the development of non-isocyanate polyurethanes based on cyclic carbonates

Recent advances in chemistry and technology of non-isocyanate polyurethane (NIPU) materials based on cyclic carbonate oligomers are reviewed in this paper. Reaction of the cyclic carbonate and amino groups results in β -hydroxyurethane fragments with specific properties. Primary attention is given to the hybrid materials that contain epoxy and acrylic compounds, especially materials based on renewable raw materials. Hybrid organic-inorganic composites comprising of silanes are also considered. An overview of the recent publications in this field is provided with a more detailed description of the Polymate Ltd. achievements. The use of NIPU materials as coatings, adhesives, and foams is described.

1. Introduction

Polyurethanes (PU) are among the most used polymers in many modern technologies [1]. However, the use of toxic components, such as isocyanates, in the manufacturing process can render PU production extremely toxic and dangerous [2]. Non-isocyanate sources for PU production have been sought for a long time.

Non-isocyanate polyurethane (NIPU) based on the reaction of polycyclic carbonates and polyamines are known for more than 50 years. Fundamentals for the practical application of NIPU on the basis of five-membered cyclic

carbonates (1,3-dioxolan-2-ones) in coatings, sealants, adhesives, etc. were largely developed by O. Figovsky in the 1970–1980's [3]. Recently, some reviews dedicated to synthesis of cyclic carbonates and NIPU have been presented [4–6]. In these works the advantages of NIPU have been described in detail.

NIPU networks are obtained by the reaction between polycyclic carbonate oligomers and aliphatic or cycloaliphatic polyamines with primary amino groups [4]. This forms a crosslinked polymer with β -hydroxyurethane groups of different structure – polyhydroxyurethane polymer. Since NIPU is obtained without using isocyanates, the process of synthesis is relatively safe for both humans and the environment in comparison to the production of the conventional polyurethanes. The model scheme of the two options β -hydroxyurethane fragments of polymer chains formed in the case of bifunctional starting materials is shown in **figure 1**.

Moreover, NIPU is not sensitive to moisture in the surrounding environment. Hydroxyl groups formed at the β -carbon atom of the urethane moiety also increase adhesion properties. Plurality of intra- and intermolecular hydrogen bonds [7, 8] as well as the absence of unstable biuret and allophanate units [9] seems to be responsible for increased thermal stability and chemical resistance to non-polar solvents.

The mechanism of the reaction of cyclic carbonates with amines, providing non-isocyanate urethanes, was studied by means of quantum chemical calculation in terms of DFT by the PBE/TZ2P method using as examples the reactions of ethylene carbonate and propylene carbonate with methylamine [10, 11]. Structural investigations have revealed four cyclic isomers with intramolecular hydrogen bond and six open conformers. This agrees well with previous results of IR and NMR spectroscopic investigations [4, 7, 8]. The reaction can proceed through the one- or multistage path involving one or two amine molecules. The second amine molecule plays the role of the catalyst of the process, resulting in a substantial decrease in the activation energy of the reaction.

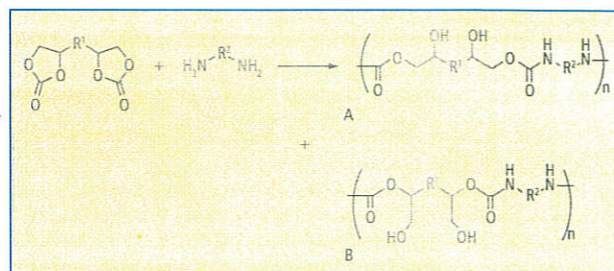
2. Brief description of recent works in the field of NIPU

A significant problem of the NIPU technologies is lack of commercially available multifunctional cyclic carbonates. Recent work in the field of new methods for preparing of cyclic carbonates is dedicated primarily to the development of new catalytic systems and the synthesis of mono-functional compounds [12, 13]. Similar catalyst systems are used also for the copolymerization of epoxides and

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Fig. 1:
 β -hydroxyurethane moieties
of non-isocyanate poly-
urethanes:
A – with secondary hydroxyl
groups;
B – with primary hydroxyl
groups



CO₂ and ring-opening polymerization of cyclic carbonates [14, 15], and one or the other direction of the reaction depends on the process conditions. For this work the synthesis of mono- and polycyclic carbonates for research purposes were provided by the company Specific Polymers, France [16].

Bernard (Rhodia) proposes a method for preparing polyhydroxyurethanes, which comprises of reacting of at least one compound (1) having a cyclic carbonate functional group and at least one hydroxyl functional group; at least one compound (2) having at least one linear carbonate functional group; at least one compound (3) having at least one primary or secondary amine functional group [17]. The subject of this invention is to position predominantly aqueous formulations on the base of polyfunctionalized polyhydroxyurethane intermediates, as well as creating a method for preparing formulations for use especially in coatings, adhesives, and others. However, the described process is very complicated and time-consuming, requires large amounts of organic solvents, and the formulations for the practical application in most cases require the use of isocyanate-containing components.

Moeller, et al. (Henkel) also describe the bonding agent system that contains a component (A) carrying at least two cyclic carbonate groups and a component (B) carrying at least two amine functional groups to prepare a two-component NIPU adhesive [18]. In this case also component (A) comprises of the reaction product of hydroxyl group-containing cyclic carbonate with an isocyanate group-containing polyurethane pre-polymer. Currently in the coatings industry cyclic carbonate raw materials are often suggested for the use in hybrid epoxy-hydroxyurethane compositions [5]. Use of such systems assumes preliminary production of adducts of the cyclic carbonates and amines. These adducts (also named as amino-urethanes) contain amine, urethane, and hydroxy groups and serve as hardeners for various oligomer compositions. Such compositions, named as Hybrid NIPU (HNIPU), are well-known in the art. Mainly they relate to waterborne epoxy compositions.

Muller-Frischinger (Huntsman Co.) [19] describes a curable composition comprising of: a) mixture of an epoxy resin a cyclic carbonate, and b) as curing agent a hybrid hardener, whereby said hardener is a blend of b1) an aminic compound, and b2) a dicyclopentadiene-phenol based Novolac. Later Muller-Frischinger et al. disclose a curable composition comprising of an epoxy resin and a hybrid hardener; wherein said hybrid hardener is a blend of adduct of amines or amidoamines and monocyclic carbonates (in particular) and a polyphenol Novolac. Such compositions are useful for rapid setting and protective coatings and adhesives in application fields like civil engineering, marine, architectural, and maintenance [20]. Also researches of Huntsman Co. proposed filled compositions on the base of NIPU or HNIPU and nanoclays [21]. In this work cyclic carbonates, synthesized by Polymate Ltd., were used as raw materials.

Klopsch et al. (BASF) disclose the use of new cyclic carbonates with unsaturated bonds as reactive diluents in epoxy resin compositions [22]. It has been found that addition of just small amounts of the new compounds to epoxy resins results in a significant increase in the reactivity of the epoxy resin composition, evident from a lower gel time following addition of a hardener. However, enhancing of other important properties has not been achieved.

Mecfel-Marczewski et al. (Construction Research & Technology GmbH) propose substituted cyclic carbonates – 2-Oxo-1,3-dioxolane-4-carboxylic acid and derivatives thereof. It is assumed that these compounds will be widely used in the oligomer technology [23]. The problem of obtaining NIPU materials based on renewable raw materials is given considerable attention in the research centers of the USA (Wilkes and co-workers, Doi, Erhan, Holser, Javni, Petrović et al.), in Poland (Rokicki and co-workers), and China (Kang, Li et al.) [5].

Recently, a number of European academic centers have begun to actively develop NIPU from the direction of plant-based raw

materials. Thus, researchers at the Institute of Macromolecular Chemistry at the University of Freiburg have investigated soy- and linseed oil-based polyurethanes prepared by curing carbonated soybean (CSBO) and linseed (CLSO) oils with different diamines [24]. Later they have reported on a very versatile new route to linear as well as crosslinked terpene-based non-isocyanate poly(hydroxyurethanes) (NIPU) and pre-polymers derived from the novel cyclic limonene dicarbonate (CL) [25]. The catalytic carbonation of epoxidized limonene with CO₂ was monitored in the presence of both homogeneous tetrabutylammonium bromide (TBAB) and heterogeneous silica supported 4-pyrrolidinopyridinium iodide (SiO₂-(I)) catalysts. The systematic variation of catalyst type, CO₂ pressure and temperature enabled quantitative carbonation in bulk and incorporation of 34.4 wt% CO₂ into CL. In contrast to conventional plant oil-based cyclic carbonates, such terpene-based cyclic carbonates afford much higher CO₂ fixation and do not contain ester groups. The absence of ester groups is essential to prevent side reaction with amines: ester groups react with the amine curing agent to afford amides and low molecular weight polyol by-products which can cause undesirable emissions and plastification of NIPU. Novel linear NIPU and prepolymers were obtained by means of CL advancement with diamines such as 1,4-butane diamine (BDA), 1,6-hexamethylene diamine (HMDA), 1,12-dodecane diamine (DADO), and isophorone diamine (IPDA).

Cramail et al. (University of Bordeaux) reported polyaddition of diamines with vegetable-based biscarbonates to prepare new polyurethanes. The intermediate material (epoxidized compounds) were obtained in two steps by a transesterification starting from monoalkyl esters of unsaturated acids and diols, and subsequent epoxidation. Then the biscarbonates were prepared from difunctional epoxides and supercritical CO₂ in the presence of ionic liquids and tetrabutylammonium bromide (TBABr) as the catalyst. Received cyclic carbonates were considered as polyhydroxyurethane precursors and further self-polycondensed with ethylene

diamine and isophorone diamine to form polyurethanes [26]. For preparation of bis-carbonates with terminal cyclic carbonate groups were used in a metathesis reaction with Hoveyda's catalyst.

Researchers from Reutlingen University and the University of Natural Resources and Life Sciences of Vienna obtained a new bio-based non-isocyanate urethane by the reaction of a cyclic carbonate synthesized from a modified linseed oil and an alkylated phenolic polyamine (phenalkamine) from cashew nut shell liquid. The incorporation of functional cyclic carbonate groups to the triglyceride units of the oil was done by reacting epoxidized linseed oil with CO₂ in the presence of a catalyst. Structural changes and changes in molar mass during the carbonation reaction were characterized. Also the aminolysis reaction of the cyclic carbonate with phenalkamine was monitored, as well as the viscoelastic properties of the system and the time of gelation [27].

A novel bio-based, isocyanate-free poly-(amide urethane) derived from soy dimer acids is described. Three steps are involved in this one-pot synthesis: first, dimer fatty acids are condensed with ethylene diamine to produce amine-terminated oligomers intermediates. These intermediates are then reacted in a second step with ethylene carbonate to yield hydroxyl-terminated di-urethanes, which then undergo a transurethane polycondensation at 150 °C for 9 h under vacuum to produce high molecular weight polymers [28]. Although the polymers are produced at a high temperature, above properties still do not allow them to find a practical application.

There is continuous development being made in the direction of silicon-contained

and nano-structured hydroxyurethane compounds. Turkish researchers synthesized a novel carbonate-modified bis(4-glycidyloxy phenyl) phenyl phosphine oxide (CBGPPO) for preparing non-isocyanate polyurethane/silica nanocomposites. Spherical silica particles were prepared and modified with cyclic carbonate functional silane coupling agent to improve the compatibility of silica particles and organic phase. The phosphine oxide-based and cyclic carbonate-modified epoxy resins and silica particles were used to prepare hybrid coatings using diamine as a curing agent. No damage was observed in the impact strength of the coatings. Incorporation of silica and CBGPPO into formulations increased modulus and hardness of the coating making the material more brittle. It was also observed, that the thermal stability of hybrid coatings enhanced with the addition of silica and CBGPPO [29].

A novel bis-urethane organosilane precursor has been developed via NIPU route in sol-gel processing conditions and employed as an organic precursor of organic-inorganic hybrid (OIH) coating systems. Coating formulations with variable proportions of this organic component were prepared and applied on aluminum substrate. These coatings were evaluated for mechanical, chemical properties and corrosion resistance and showed some improvements [30].

Hanada et al. disclose a polysiloxane-modified polyhydroxy polyurethane resin being derived from a reaction between a five-membered cyclic carbonate polysiloxane compound (fig. 2) and an amine compound, its production process and a resin composition. New materials can be used for thermal recording medium, imitation leather, thermoplastic polyolefin resin skin material, weather strip material, and weather strip [31].

3. Recent achievements of Polymate Ltd.

3.1 Polyhydroxyurethanes

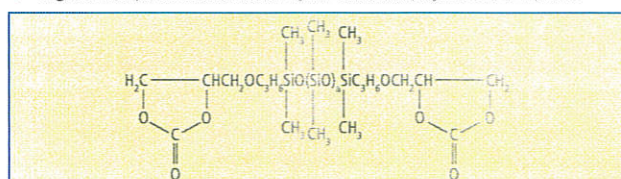
Usually polyhydroxyurethane polymers have poor water resistance due to the plurality of hydroxyl groups. It is however possible to prepare water-resistant materials in some formulations. For example, on the base of acrylic epoxy oligomers, cyclocarbonate acrylic polymers with high water and weather stabilities were prepared. A paint was developed with curing temperature 110 °C, in 2–3 hours. Unfortunately we need to use solvents for this composition [4].

Polymate Ltd. recently started works on the synthesis of aliphatic multifunctional cyclic carbonates from corresponding epoxies and carbon dioxide and NIPU based on them. The authors tested some compositions of polyfunctional carbonates synthesized in the laboratory, namely trimethylol propanetri-cyclocarbonate (TMPTCC) and chlorine containing aliphatic tricyclocarbonates (on the base of chlorine containing aliphatic epoxy resins Oxilin) and various diamines: 2-methylpentamethylene diamine (MPMD) – Dytek A, Invista Co.; meta-xylenediamine (MXDA) – Mitsubishi Gas Chem. Co.; polyetheramine Jeffamine EDR-148 – Huntsman Co.; diethylenetriamine (DETA) – D.E.H. 20, Dow Chemical Co. Properties of these materials are shown in table 1. Some of the results are significantly higher than previously achieved levels and offer good prospects for their practical use. Further elaboration will be undertaken.

3.2 Hybrid non-isocyanate polyurethanes

Recently the authors proposed compositions based on oligomer systems which contain

▼ Fig. 2: Example of five-membered cyclic carbonate polysiloxane compound



▼ Tab. 1: Properties of polyhydroxy urethanes

CC	Amine	Tensile strength / MPa	Elongation / %	Water absorption / %
TCCTMP	MPMD	33–47	3.3–3.8	n/a
CC Oxilin 5	MXDA	18	4	n/a
CC Oxilin 6B	EDR-148	0.8	10	4.0
CC Oxilin 5	DETA	1.6	15	n/a

hydroxy-amine adducts on the base of aliphatic mono- and polycyclic carbonates (Cycloate A) as hardeners [32]. This composition was used for 100 % solid flooring coating with high abrasion resistance and mechanical properties. Thus, Polymate has developed practically used formulations on the basis of HNIPU, using the two formulations F1 and F2 shown in **table 2**.

3.3 Hydroxyurethane modifiers (HUM)

A separate area of the use of NIPU technology is in the preparation of pure hydroxyalkyl urethane compounds. All known polymer compositions with hydroxyalkyl urethane monomers require specific chemical reactions (such as transesterification, transamination, or self-crosslinking). These reactions are

carried out at elevated temperatures, in the presence of organic solvents, and/or in water-dispersion media, sometimes in the presence of catalysts [5]. The authors recently proposed a novel concept of generating new multifunctional modifiers. The HUM, which possesses a wide range of hydrogen bonds, is embedded in an epoxy polymer network without a direct chemical interaction.

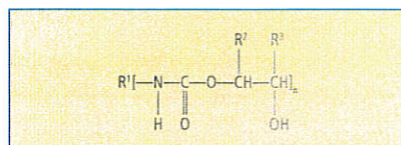
Our patent application [33] discloses a novel "cold" cure epoxy-amine composition modified with a hydroxyalkyl urethane (HUM), which is obtained as a result of a reaction between a primary amine (C1) and a monocyclocarbonate (C2), wherein modifier (C) is represented by the formula in **figure 3**, wherein R1 is a residue of the primary amine, R2 and R3 are the same or different and are selected from the group consisting of H, alkyl, hydroxyalkyl, and n satisfies the following condition: $n \geq 2$. Diluents, pigments, and additives can be used. The new modifier primarily affects a significant acceleration of the curing process as well as an increase in abrasion resistance. Doping with the HUM imparts to the cured composition superior coating performance

characteristics (pot life/drying, strength-stress properties, bonding to a variety of substrates, appearance in a well-balanced state). Since the structure of the polymer network is not broken, other characteristics, such as weathering and chemical resistance, do not worsen. The dependences of curing characteristic and abrasion resistance from content of HUM-01 are shown in **figure 4** [34]. The following sections provide examples of successful applications of HUM into other oligomeric systems.

3.4 Hydroxyurethane compounds from renewable plant-based raw materials

Recently authors proposed a new method of producing a hybrid polyhydroxyurethane network comprising of [35]: (a) reacting epoxidized unsaturated fatty acid triglycerides with carbon dioxide in the presence of a catalyst to obtain carbonated-epoxidized unsaturated fatty acid triglycerides, wherein conversion of oxirane groups to 2-oxo-1,3-dioxolane groups (cyclic carbonate groups) for said carbonated-epoxidized unsaturated fatty acid triglycerides ranges from 35 % to 85 % (see **figure 5**);

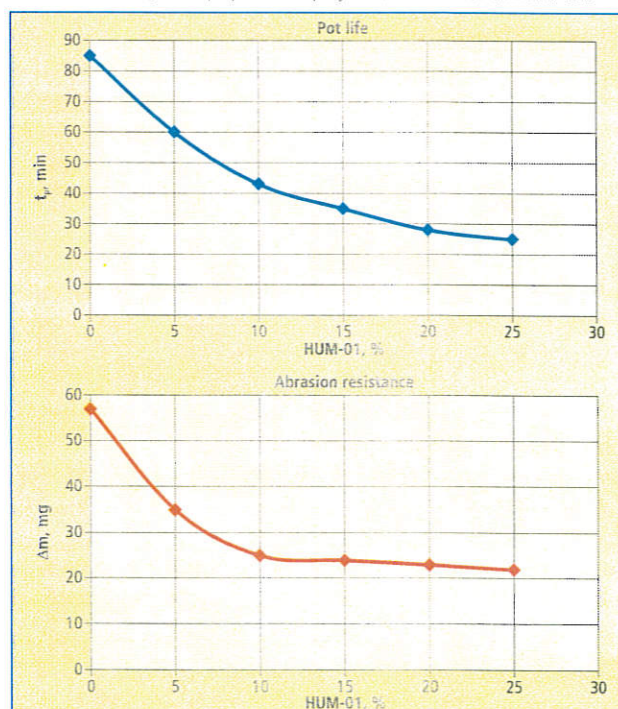
Fig. 3: Basic formula of hydroxyalkyl-urethane modifier (HUM)



Tab. 2: Composition and properties of flooring compounds

Composition	Parts by weight	
	F1	F2
Hydroxyl-amine adduct "1" (on the base of Cycloate A)	50.0	–
Hydroxyl-amine adduct "2" (on the base of Cycloate A)	–	50.0
Epoxy resin D.E.R. 324 of Dow Chemical	45.0	40.0
Polycyclic carbonate Cycloate A	5.0	–
Reactive acrylic oligomers (mixture) of Sartomer	–	10
Titanium dioxide	5.0	5.0
Carbon black	–	0.1
BYK-A530 (surface active additive of Byk Co.)	2.0	–
BYK-320 (surface active additive of Byk Co.)	–	1.5
Properties	Values	
Mixed viscosity, 25 °C, mPa·s	1,450	970
Pot life, 25 °C, min	30–60	30–60
Tack free, 25 °C, h	4	6
After seven days room temperature, substrate – concrete		
60° film gloss	100–105	115–120
Hardness / Shore D	70–80	70–80
Tensile strength / MPa	50–60	60–70
Elongation at break / %	5–7	3–4
Taber abrasion, 1,000 cycles/1,000 g, CS-17 wheel / mg	27	29
Impact resistance / N.m, ≥	20	20

Fig. 4: Influence of modifier HUM-01 (trimethyl-hexamethylene-diamine + propylene carbonate) on the properties of epoxy composition based on D.E.R. 331



(b) mixing and reacting the carbonated-epoxidized unsaturated fatty acid triglycerides with a compound having an amine functionality comprising at least one primary amine group realized at stoichiometric or within nearly balanced stoichiometry; (c) mixing and reacting the product of (b) with a compound having amine functionality comprising at least two primary amine groups realized at excess of an amine-functional compound; (d) mixing the product of (c) with a compound having amino-reactive groups and selected from the group comprising: (1) a compound having epoxy functionality, and (2) a mixture of the compound having epoxy functionality with carbonated-epoxidized unsaturated fatty acid triglycerides, a ratio of the sum of amino-reactive groups to the sum of amine groups being stoichiometric or within nearly balanced stoichiometry; and (e) curing the resulting composition at ambient temperature. The proposed method can significantly reduce time of synthesis and improve quality of the final products.

3.5 Silane-containing and nano-structured hydroxyurethane compounds

The concept of generating silica from alkoxysilanes by the sol-gel method within a macromolecular organic phase (in situ) is widely known in the art. The organic and inorganic components of these materials are present as co-continuous phases of a few nanometers in lateral dimensions. Earlier authors have studied new types of NIPUs based on cyclic carbonate-epoxy resin systems and aminoalkoxysilanes [36]. The proposed dendro-aminosilane hardeners give the possibility for the introduction of siloxane fragments into the aromatic structure of BPA epoxy-amine and cyclocarbonate network polymers which improves the service properties of the network polymer. Additional hydrolysis of organosilane oligomers creates a secondary nano-structured network polymer.

Known in the art as hybrid organic-inorganic compositions include mixtures of epoxy resins, amine hardeners, functional silanes, and/or polysiloxanes and cure in the presence of water in an amount sufficient to bring about substantial hydrolytic polycondensation of the silane [5].

A novel nano-structured hybrid polymer composition was synthesized on the base of epoxy-functional components, cyclic carbonate components, amine-functional components, and acrylate (methacrylate) functional components, wherein at least one epoxy, amine, or acrylate (methacrylate) component contains alkoxysilane units [37]. The composition is highly curable at low temperatures (approximately 10–30 °C) with generating nanostructure (fig. 5) under the influence of the forming of active, specific hydroxyl

groups by reaction of cyclic carbonates with amine functionalities. These hydroxyurethane functionalities activate by hydrolytic polycondensation of alkoxysilanes by means of atmospheric moisture, thus producing an organic-inorganic nanostructure without a special procedure of water embedding or addition of nanofillers. The cured composition (fig. 6) has excellent strength-stress properties, adhesion to a variety of substrates, appearance, and resistance to weathering, abrasion, and solvents.

Fig. 5: Obtaining carbonated epoxidized unsaturated fatty acid triglycerides

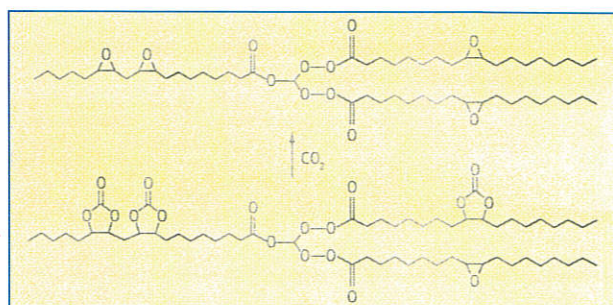
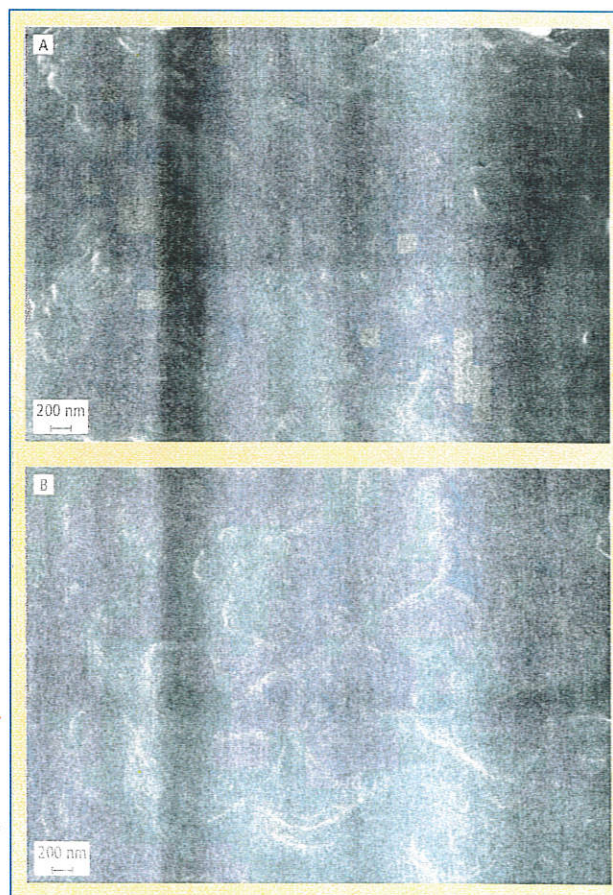


Fig. 6: Images of the fractured surfaces of the cured compositions at 20,000x magnification (Auriga Cross-Beam): A – neat epoxy-amine composition; B – epoxy-silane-amine composition



3.6 Sprayable foam

The vast majority of methods for the application of sprayable polymer foams onto various substrates use air or airless spraying equipment. The main advantage of these methods is the rapid formation of a polymer structure to obtain a non-flowing foam on vertical surfaces. However, non-isocyanate resin foams require some other approach since they exhibit longer durations of gelation and solidification, which can lead to flow on vertical surfaces and a collapse of the foam.

Recently, Olang (Owens Corning) disclosed hybrid spray foams that use a urethane reactant, a crosslinker, and an (optional) epoxy and/or acrylic resin, along with a blowing agent and rheology modifier to produce a quick-setting foam that remains in place until the foam forms and cures [38]. In some other formulations the author used the NIPU

adducts of cyclic carbonates and di- or polyamines, received from Polymate. Unfortunately, the use of rheology modifiers in practice increases the viscosity of the compositions and imparts to them a thixotropic property, which significantly limits the use of this method for spray foams.

Earlier, we described some non-isocyanate compositions related to hybrid systems on the basis of epoxy, hydroxyurethane, acrylic, cyclic carbonate, and amine raw materials in different combinations. Patent [39] discloses foamable, photopolymerizable liquid acrylic-based compositions for sealing applications, which include products of reaction of non-isocyanate urethane diols with methacrylic or acrylic anhydride. Patent [40] describes hybrid non-isocyanate foams and coatings on the basis of epoxies, acrylic epoxies, acrylic cyclocarbonates, acrylic hydroxyurethane oligomers, and bifunctional amines. However, all these compositions are used

"in-place" (in situ) and are unsuitable for spray applications.

Finally, Polymate has developed a basic formulation and technique for mixing and foaming insulating spray foam and a procedure for obtaining conventional foams has been updated in respect to HNIPU application [41]. Technical specifications of this newly developed composition correspond to the mean values of a similar urethane-based thermal insulation. The ultimate strength of the new material is about 1.5 times higher than that of the polyurethane foam, and the heat-insulating properties are at the same level as in polyurethane foam with open cell structures. The possibility of application by spraying was tested on pilot equipment.

Recently the composition of the foam was studied with regards to the use of renewable raw materials, including new HUM. As a result, hard and elastic foams were obtained with properties not inferior to polyurethane foams. The foams were produced in the laboratory only but offered reasonable properties (tab. 3). Research and development of new foams is expedient and can be continued.

3.7 UV curable HNIPU floorings and coatings

The photochemistry involved in UV curable materials is very complicated and usually is tailored to the specific process with its method of application, UV source, pigments, and desired properties of the cured material. UV curable concrete floor coatings offer a durable, high-performance and eco-friendly opportunity for HNIPU chemistry. These thin-film coating systems cure instantly, thereby minimizing the downtime of any facility. Other benefits include excellent chemical resistance, easy cleanability, little odour, and the ability to coat in cold conditions.

The surface preparation and application of UV coatings is similar to that of traditional concrete floor coatings. UV coating systems include both clear and pigmented systems. The clear system consists of a primer and a topcoat, which is available in different finishes ranging from high gloss to matte. The

▼ Tab. 3: Rigid HNIPU foam

Properties	Standard	Rigid foam insulation
Viscosity (Brookfield RVDV II, Spindle 29, 20 rpm) at 25 °C, cP	ASTM D2393	2,800–3,200
Base "A"		3,600–4,100
Base "B"		≤3,700
"A" + "B" (3–5 s after mixing)		
Pot life at 25 °C (77 °F) / s		8–10
VOC	ASTM D2369	Compliant
Gel time / s		2–4
Touch dry / s		30–40
Curing for transportation / min		15–20
Appearance of rigid foam		White
Compressive properties of rigid cellular plastics, 24 h / MPa	ASTM D 1621	0.2–0.4
Apparent density of rigid cellular plastics / kg/m ³	ASTM D2794	30–40
Thermal transmission properties by means of the heat flow meter apparatus, h·ft ² ·°F / Btu·in	C 518	4.5–5.0

▼ Tab. 4: Properties of HNIPU UV-cured flooring compared to conventional UV-cured flooring

Properties	Standard	Conventional UV-cured flooring	HNIPU UV-cured flooring
Adhesion	ASTM D 3359-07, B	3B	5B
Pencil hardness	ASTM D 3363-05	5H	4H
Solvent resistance	ASTM D5402-06	200+	200+
Gloss	ASTM D 523	84	90
Abrasion resistance, CS-17, 1,000 g, 1,000 cycles, mg	ASTM D1044	150–200	100
Thickness applied / mm		0.066–0.1	0.3–0.8
Primer		Required	Not required for properly prepared substrates
Number of layers		2+	1

topcoat finish can be further enhanced by broadcasting additives for decorative or performance purposes.

Single-coat systems are also available. The thin film thickness can range between 0.3 mm and 0.8 mm. Unlike conventional UV curable coatings, formulations developed by Polymate Ltd. contain up to 60 % of vegetable oil derivatives, such as modified soybean oil. This creates a composition with higher elasticity while maintaining the basic strength characteristics. The use of these compounds improves the adhesion of the cured composition to concrete, allowing reduction in the number of coating layers to two, and for special coatings even to a single layer. The uniqueness of this compound is the possibility to apply one layer up to 0.8 mm thickness, at the rate of polymerization which allows the use of standard curing technology and standard equipment. The introduction of the new hydroxyurethane modifier (HUM) based on vegetable raw materials and adducts obtained on its basis allow improving hardness and wear resistance, while maintaining the other properties of the system (tab. 4).

The uniqueness of the developed formulation and the possibility of coating concrete sometimes without a primer, with a layer thickness of 0.3–0.8 mm allows the covering of even open areas. Application is done by spraying, eliminating the negative effects of sunlight during the coating process and uses sunlight during the curing process, which reduces the total polymerization time even more.

4. Conclusions

Many well-known companies and research centres around the world are developing new methods for the synthesis of cyclic carbonates and compositions thereof. A leading position in the development of non-isocyanate materials is being held by the research center Polymate Ltd. The authors believe that further developments in the field of polyhydroxyurethanes, that offer the most promising directions for future research include:

- Creation of production of polyfunctional cyclocarbonates, development of optimal technology and equipment: carbonized vegetable oils and terpenes; carbonized aliphatic compounds, including chlorinated ones; and carbonized polyfunctional silicones.
- Development of waterborne HNIPU formulations.
- Development of NIPU formulations for sealants and adhesives.
- Development of production of amines modified with hydroxyurethane groups.
- Elaboration of non-amine RT curing agents for oligomer compositions.
- Development of self-extinguishing compositions of HNIPU.
- Development of silicone-based HNIPU.
- Development of NIPU and HNIPU-based foams.
- Development of formulations for UV-cured compositions.

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